Discrepancies between MICS-Asia III Simulation and Observation for Surface Ozone in the Marine Atmosphere over the Northwestern Pacific Asian Rim Region

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Abstract. In order to identify the causes of overestimate of the surface-level O_3 mixing ratio simulated by three regional chemical-transport models, NAQPMS v.3 (abbreviated as NAQM in this paper), CMAQ v.5.0.2, and CMAQ v.4.7.1, compared to the EANET observational data at a marine remote site at Oki in July 2010, analyses of hourly data of O_3 mixing ratios and net ozone production were made in the context of MICS-Asia III. In addition to Oki, model-simulated and observational data for two other EANET marine sites, Hedo and Ogasawara, were also examined. Three factors, i.e., long-range transport from the continent, in-situ photochemical formation, and dry deposition of O_3 on seawater have been found to contribute to the overestimate by these regional models at Oki. The calculated O_3 mixing ratios during long-range transport from the continent were much higher for all the three models than those of the observation. In-situ photochemical formation, demonstrated by a distinct diurnal variation which was not discerned in the observational data, was seen in the simulated data of all the three models and ascribed to the virtual transport of NO_x from the southern urban areas of the main island of Japan. At Hedo and Ogasawara overestimate of O_3 in oceanic air mass was found for CMAQ v.5.0.2 and v. 4.7.1, while the agreement was much better for NAQM. The overestimate by CMAQ models were

inferred to be due to the use of too small dry deposition rate of O_3 compared to NAQM in the Northwestern Pacific. However, the dry deposition velocity of O_3 in the Bohai Bay and the Yellow Sea has been assumed to be comparable to that of the open ocean in all the three models, which could have resulted in the overestimate of O_3 mixing ratios in this area and also in the long-range transport of O_3 from the continent to Oki. A higher value of dry deposition velocity in this marine area is expected considering the higher content of organics in the surface sea layer brought by rivers and atmospheric wet deposition. Empirical measurements of the mixing ratios and dry deposition flux of O_3 in this area is highly recommended, since it would affect the simulated mixing ratios in the down-wind region in the Pacific rim region.

1 Introduction

Surface ozone simulation by regional chemical transport models (CTMs) has become widely used and is thought to be well-developed considering its long history since the 1980s (e.g. De Wispelaer, 1981) and a well-established underlying fundamental science of tropospheric gas-phase photochemistry (e.g. Akimoto, 2016). Nevertheless, a recent model intercomparison study, MICS-Asia III, has revealed a large variability in the simulated spatial distribution of surface ozone (O_3) mixing ratios in the East Asian region among models and between models and observations (Li, J. et al., 2019). Since regional CTMs are commonly used for proposing mitigation policies on how to reduce the emissions of NO_x and NMVOC for controlling photochemical ozone pollution, there is an urgent need to provide useful information on advancing the current understandings of discrepancies among the models and between modeled and observed mixing ratios of O_3.

We realize that model intercomparison studies of ozone simulation for air quality is at the stage of identifying the causes of discrepancies and depicting the problem that are used to improve models, rather than simply demonstrating the statistical performance of the models and showing the degree of agreement between the simulated ensemble mean and observations. Our previous paper in this special issue (Akimoto et al. 2019), noted a disagreement between the observed mixing ratios of surface O_3 in the megacities of Beijing and Tokyo and at a remote oceanic site at Oki, and those simulated by three selected regional models, namely WRF-CMAQ, v.5.02 and v.4.7.1, and WRF-NAQPMS v.3. As for the urban areas of megacities, we found that the degree of agreement of the simulated levels of O_3 and NO with the observations were strongly coupled, and we discussed the importance of making comparisons of simulated mixing ratios of precursors (NO_x and NMVOC) together with O_3 itself. Specifically, we proposed to confirm the potential importance of the heterogeneous "renoxification" reaction of HNO_3 to regenerate NO_x on the aerosol surface by comprehensive field observations of NO_y. We also identified that the difference in the vertical transport scheme affected the simulated results of O_3 significantly.

As for the marine remote site of Oki, an island in the western part of the Sea of Japan, an overestimate of O_3 by ca. 20 ppbv compared to observations in July 2010 has been noted for all the three selected models. However, the causes of the disagreement between the models and observations were not discussed in the previous paper (Akimoto et al. 2019). Oki is one of the baseline sites for O_3 observations, and the O_3 level there reflects the amount of transboundary long-range transport of O_3 from the Asian continent to the Pacific rim region. It is also a reference "background" site for air quality in Japan. Therefore, a better matching between observational data and model simulation is desired, and elucidation of the causes of the overestimates by the

models is worth pursuing.

So far, validations of surface O_3 in the oceanic area by regional CTMs have rarely been made. This is because regional CTMs have been applied mainly to the air quality in urban polluted areas with the aim of controlling precursor emissions. However, in the East Asian Pacific rim region, the continental outflow over the ocean is transported to the downwind land area, thus, a discussion of transboundary pollution is necessarily needed to validate over the oceanic area. In the marine region the dry deposition of O_3 on the oceanic water is one of the important parameters which would affect the mixing ratios of O_3 in the marine boundary layer. An intensive evaluation of ozone deposition simulations using regional models in East Asia has been reported by Park et al. (2014), but the detailed analysis has been made mostly on land area and the discussion in marine region is limited.

On the other hand, since the oceans cover 2/3 of the earth surface, the air-sea exchange plays an important role in the tropospheric ozone budget, and substantial discussions on the impact of dry deposition of O_3 over oceanic water have been made by global CTMs (e.g., Ganzeveld et al., 2009; Young et al., 2013; Hardacre et al., 2015; Luhar et al. 2018) . According to the recent estimate, the ozone dry deposition of O_3 is found to be 98 ± 30 Tg yr^{-1} for the ocean, about 13% of the global deposition of 723 ±87 yr^{-1} (Luhar et al., 2018) in contrast to the total global total dry deposition of 1094 ± 264 Tg yr^{-1} (Young et al., 2013) of which about 35% is to the ocean (Ganzeveld et al., 2009; Hardacre et al., 2015). Hardacre et al. (2015) observed that ozone dry deposition to the water surface in models has the largest uncertainty compared to other surface types.

According to the O_3 overview paper of MICS-Asia III by Li, J. et al. (2019) (Figure 3(i)), substantial overestimate of the mixing ratios of O_3 at Oki was revealed only in summer to early autumn (June to September) by most of the 13 submitted models. In the present study, we made a comparison of the simulated and observational O_3 data in July when the highest overprediction has been revealed. Among the models, CMAQ v.5.0.2 and v.4.7.1 and NAQM v.3 has been analyzed just as same as in our previous paper (Akimoto et al., 2019) due to the availability of hourly data and process analysis data. We made a comparison of the simulated and observational O_3 data in the marine atmosphere over the Northwestern Pacific Asian Rim Region. In addition to Oki, comparisons at two other oceanic sites, Hedo and Ogasawara which are even more remote than Oki, have been performed. Among the selected three observational sites, Ogasawara was categorized as “true oceanic site” in the Northwestern Pacific (Schultz et al., 2017), Oki is a marine site affected more often by the continental outflow even in the summer, and Hedo is characterised between the two sites.

2 Models and Observational Sites

The selected three models are the same as those in our previous paper, i.e., WRF-CMAQ v.5.0.2, v.4.7.1, and WRF-NAQPMS v.3 (abbreviated as NAQM hereafter in this paper). Model calculations by the CMAQ v.5.0.2, v.4.7.1, and NAQM were conducted at the University of Tennessee (USA), National Institute for Environmental Studies (Japan), and Institute of Atmospheric Physics (China), respectively. Basic features and the simulated domain of these regional models have been given in previous papers in this special issue (Akimoto et al., 2019; Li, J. et al., 2019). Briefly, the employed horizontal resolution was 45 km for all the models. The models employed the common meteorological fields from WRF simulations and common emissions of MIX (0.25°× 0.25°) for 2010 (Li, M. et al., 2017) both developed in the MICS-Asia III project. A detailed description about the WRF simulation can be found in Li et al. (2019) and Kong et al. (2020). Briefly, it was nudged toward the final analysis dataset from the National Centers for Environmental Prediction and National Center for Atmospheric Research (NCEP/NCAR). Dry deposition schemes by Wesely (1989) and M3DRY (Pleim et al., 2001) were used in NAQM and CMAQ, respectively. The initial and boundary conditions were supplied by global models, CHASER for CMAQ v.4.7.1 and NAQM, and GEOS-Chem for CMAQ v.5.0.2. The two global models used Wesely (1989) as a dry deposition scheme.

Fig. 1 shows three observational sites of EANET (Acid Deposition Monitoring Network in East Asia) at Oki (36.3°N, 133.2°E, 90m asl), Hedo (26.9°N, 128.2°E, 60m asl), and Ogasawara (27.1°N, 142.2°E, 212m asl) (www.eanet.asia/about/site information/) which were selected for the comparison of observational data with model simulation. The Oki station is on the northern cliff of Dogo Island of Oki Islands, the Hedo station is at Cape Hedo located at the northern tip of Okinawa main island, and the Ogasawara station is on the hill of Chichi Island of Ogasawara Islands. Measurements of O_3 were made by using UV absorption instruments (Horiba APOA-360, -370). The observational data used for the three sites were the 1-hr averaged values in July 2010, provided by the EANET Network Center, Asia Center for Air Pollution Research (ACAP) (http://www.acap.asia). Fig. 1 also shows the monthly averaged wind field in July.

Fig. 1

3 Results and Discussion

3.1 Comparison of O_3 at Oki, Hedo, and Ogasawara

Figures 2(a)-(c) depict the comparison of the monthly mean diurnal variation of surface O_3 mixing ratios in July 2010 between the model simulations and observations at Oki, Hedo, and Ogasawara, respectively. The data shown in Fig. 2(a) at Oki is the same as that presented in our previous paper

Fig. 2

(Akimoto et al., 2019), and indicates that the O_3 mixing ratios simulated by all three models fall within the range of ~10 ppbv at the 52–71 ppbv level, as compared to the observational value of 34–43 ppbv. Thus, all three models overestimated the O_3 mixing ratio by nearly 20-30 ppbv. A monthly averaged diurnal amplitude of 17 and 15 ppbv with a daytime maximum and a nighttime minimum can be noted for CMAQ 5.0.2 and NAQM, which is substantially larger than the variability of 7 and 9 ppbv for the simulation by CMAQ 4.7.1 and the observation, respectively.

In contrast to Oki, the monthly-averaged observational mixing ratios of O_3 at Hedo and Ogasawara are approximately in the same range, 12-16, and 10-14 ppbv, respectively, with a slight diurnal variation of ca.4 ppbv. The monthly averaged mixing ratios of O_3 at 10-15 ppbv in July is typical in the marine boundary layer at these remote islands (Pochanart et al., 2002), which are basically under the influence of Pacific oceanic airmass as shown by the wind field in Fig. 1. The model simulation of NAQM reproduced well the monthly-averaged O_3 levels at these sites with a slight diurnal variation (ca. 4 and 1 ppbv at Hedo and Ogasawara, respectively). Meanwhile, CMAQ 5.0.2 and 4.7.1 agree well with each other, but overestimate the observed monthly-averaged O_3 mixing ratios by nearly 23-27 ppbv at Hedo and 11-14 ppbv at Ogasawara. These models show a diurnal variation of 9-16 ppbv at Hedo, which is much larger than the observation. The diurnal variation revealed by these models at Ogasawara is less than 1 ppbv, agreeing well with NAQM.

In order to clarify the causes of the discrepancies, comparisons of the mixing ratios of O_3 on an hourly basis were made at Oki, Hedo, and Ogasawara (Figs. 3(a)-(c)). In the observational data at Oki shown in Fig. 3(a), minimum mixing ratios of ca. 20 ppbv are often seen within a short time duration of a few hours, which represents the O_3 level in the marine air mass brought by the southerly wind of the summer monsoon from the surrounding oceanic area near Japan, as revealed by Akimoto et al. (1996). The observational data also shows that the O_3 mixing ratio at Oki often reaches the level of ca. 60 ppbv, and the highest O_3 level of ca. 80pbv was observed on July 6-8. This event is thought to be caused by the long-range transport from the continent (Akimoto et al., 1996). The model simulations captured this event, but the estimated peak height of O_3 on July 6-7 is much higher, more than 130 ppbv by CMAQ 5.0.2, and ca 100 ppbv by NAQM and CMAQ 4.7.1.

Fig. 3

As seen in Fig. 3(a), a distinct diurnal variation with a daytime maximum and a nighttime minimum can be discerned during July16-20 in the simulations by NAQM and CMAQ 5.0.2. The diurnal variation is less profound in the CMAQ 4.7.1 simulation and is not discernible in the observational data. This feature apparent in the model simulations is thought to be the result of in-situ photochemical O_3 production during daytime, caused by overestimated NO_x mixing ratios by the models, as will be discussed later in **3.3**.

At Hedo on Okinawa island, the observation shows that the minimum (baseline) mixing ratio

of O_3 in the maritime air mass in this region is 5-10 ppbv in July (Fig. 3b). The figure also shows that the observational O_3 level frequently reaches 20-30 ppbv. NAQM reproduced well the background marine O_3 levels of ca. 10 ppbv and the higher O_3 levels of 20-30 ppbv. In contrast, a strong diurnal variation is apparent in the CMAQ 5.0.2 simulation with an amplitude of more than 20 ppbv, and also in the CMAQ 4.7.1 simulation with a slightly less amplitude. Furthermore, the maritime background O_3 level simulated by these models is ca. 20 ppbv, nearly 10 ppbv higher than the observation. These values of the diurnal variation and background level clearly bring an overestimate of monthly mean O_3 levels by more than 20 ppbv (Fig. 2(b)).

At Ogasawara, a more remote site in the Northwestern Pacific about 1000 km south of Tokyo, the observational O_3 mixing ratios in the oceanic air are 2-8 ppbv (Fig. 3(c)). However, even at Ogasawara in summer, higher O_3 mixing ratios up to 30 ppbv have been observed. The less than10 ppbv baseline level of O_3 in the remote oceanic air in this region is well reproduced by NAQM, but CMAQ 5.0.2 and 4.7.2 give more than 10 ppbv higher values than the observation. All three models captured well the observed O_3 peak on July 23-24, which can be ascribed to long-range transport from Japan, as will be discussed in **3.2** below. NAQM reproduced well the observed maximum O_3 mixing ratio of ca. 30 ppbv as well as the transport amplitude of ~25 ppbv. CMAQs gave the similar amount of O_3 increase due to the transport, ~25 ppbv, but the overestimated the peak values due to the overestimate of the baseline mixing ratios. A certain feature of diurnal change peaking at daytime can be seen in both observation and model simulations for several days in Fig. 3(c). Although Ogasawara is generally thought to be a real background site based on its remote location over the open Pacific ocean, the monitoring station is actually surrounded by trees, and the data may be affected by local emissions of biogenic VOCs and soil NO_x, which may possibly cause some photochemical activity to form in-situ O_3 under certain meteorological conditions. Overall, the NAQM-simulated values of monthly mean mixing ratios match to the observations, and the CMAQ 5.0.2 and 4.7.1 simulations give ca. 15 ppbv higher O_3 values at Ogasawara in July (Fig. 2(c)).

From these results, we consider that three factors, long-range transport, in-situ photochemical O_3 formation, and background mixing ratio of oceanic O_3 which is affected by dry deposition of O_3 on seawater, would be related to the overestimate of surface O_3 at Oki in July by the selected three models.

3.2 Long-range transport of O_3

At least two high O_3 events, one at Oki between July 6-8 and the other at Ogasawara on July 23 and 24 are thought to be caused by long-range transport of O_3. In order to confirm the characteristics of these events, the spatial distribution of surface O_3 in East Asia obtained by

NAQM, CMAQ 5.0.2 and 4.7.1 at 18 JST (Japan Standard Time) on July 6 and at 19 JST on July 23, are shown in the left and right figures in Figs. 4(a)-(c), respectively. Fig. 4(a)-(c) (left-hand) shows the event that the plume of continental outflow is transported to the Yellow Sea, South Korea and Japan covering the Oki site. In this event, the simulated surface O_3 mixing ratios by NAQM, CMAQ 5.0.2 and 4.7.1 are 104, 135 and 110 ppbv, respectively, which are substantially higher than the observational value of 80 ppbv. An overestimate of the O_3 level in the upwind area of Beijing produced by CMAQ 5.0.2 and 4.7.1 has been identified in our previous paper (Akimoto et al., 2019), which may have contributed to some extent to the overestimate of O_3 by these models during this event. The reduction of overestimate over the continent would remove the substantial part of the overestimate of O_3 on these days although the sensitivity analysis has not been made in the present study. On the other hand, NAQM reproduced reasonably well the O_3 levels in the urban areas of Beijing in July (Akimoto et al., 2019). Nevertheless, the simulated level of O_3 by NAQM during the event is ca. 20 ppbv higher than that of the observation, which implies that an additional factor contributes to the overestimate of O_3 in the long-range-transported air mass.

Fig. 4

This additional factor of the overestimate of surface O_3 in the long-range-transported O_3 from the continent commonly affecting the results of all of the three selected models could to be the result of the overestimate of surface O_3 over the Bohai Sea, Yellow Sea, and the southern part of the Sea of Japan caused by the underestimate of dry deposition velocity of O_3 over the seawater in these areas, which will be discussed later in detail in **3.4**.

The right-hand figures in Fig. 4(a)-(c) shows the long-range transport of O_3 over Japan to the Ogasawara islands on July 23. Under certain meteorological conditions, a high level of O_3 over Japan is transported southward toward the Pacific Ocean. The simulations of the increment of transported O_3 to Ogasawara by all the three models reproduce the observed value of ~25 ppbv reasonably well, and the long-range transport of O_3 from Japan in this region is not overestimated in either of the models.

3.3 In-situ photochemical formation of O_3

An apparent diurnal variation of O_3 with a daytime maximum and a nighttime minimum have been noted in the simulated results at Oki in Fig. 3(a) for all three models particularly during July 16-23, which is not discerned distinctly in the observational data. Such a diurnal variation in the simulated results strongly suggests that an in-situ photochemical buildup of O_3 occurs in the model simulations. In order to assess the extent of the photochemical buildup and net chemical production of O_3 at the remote marine site of Oki, Figures 5(a) and (b) compare the model-simulated mixing ratio of NO_2 and NO with those of NO_2* and NO observed using a

Fig. 5

chemiluminescent analyzer with Molybdenum (Mo) catalyzer. Since the Mo catalyzer reduces not only NO_2 but also gaseous HNO_3 and particulate NO_3^- to NO in an unstoichiometric way, the quantity of NO_2^* rather than NO_2 is reported in the EANET protocol. Since the contribution of HNO_3 to NO_2^* is significant at remote sites, it is not possible to assess the exact ratio of NO_2/NO_2^*, thus, NO_2^* should be used only as a rule of thumb for the upper limit of NO_2.

As can be seen in these figures, all the simulated data show significant levels of NO_2 over 2 ppbv in the period from July 16 to 21, which is substantially higher than the observed NO_2^* which is typically lower than 2 ppbv. It should be noted that the temporal variation of NO_2 in the simulations by CMAQ 5.0.2 and 4.7.1 is similar, but the absolute mixing ratio simulated by CMAQ 5.0.2 is substantially higher than that simulated by CMAQ 4.7.1. Meanwhile, the temporal pattern of the NO_2 mixing ratios simulated by NAQM is quite different from that simulated by CMAQs, and a significantly high level of NO_2 up to 11 ppbv can be seen on July 13.

It should be pointed out that Oki station is a remote site and the emission of NO_x within the model grid covering Oki is very low, which gives a low simulated mixing ratio of NO_2 of less than 1 ppbv in the early half of the month by all the models. Since all three models use the same emission data supplied by the MICS-Asia III project (Li, M. et al.2, 2017), the high NO_2 over 5 ppbv in Figs. 5(a) typically seen in the latter half of the month is thought to be transported from urban/industrial sources nearby. A possible source is Matsue and surrounding cities in mainland Japan which are located less than 100 km south of the Oki site. Model simulations of meteorology may produce a high NO_x value from this area, which does not happen in reality. The different temporal pattern of NO_x between the NAQM and CMAQ simulations is thought to result from the difference in the coupling of transport and chemistry in these models. A high NO_2/NO ratio seen in the model simulation is consistent with the estimate that the virtual source area of NO_x is not close to the site on the island. Similar figures as Fig 5(a)-(b) for Hedo and Okinawa are given in Figs, 5S-1 and 5S-2 (supplement), respectively. Although Hedo is a remote island site, the area surrounding the station consists of sugar cane field soils emit substantial NO (Matsumoto et al., 2001), which would give ≤~0.5 pptv level of NO in observational data for certain days. The MIX emission inventory used for the modeling considers agricultural sources of NO_x without specifying crop species. Diurnal variation of NO_2 with a smaller amplitude (≤~4 ppbv) than Oki is seen at Hedo for CMAQ 5.0.2 and 4.7.1, but not for NAQM. At Ogasawara none of the model shows NO_2 peaks more than 0.5 ppbv.

Figures 6(a)-(c) depicts the hourly net chemical production of O_3 at Oki, Hedo and Ogasawara in July, respectively, calculated by NAQM, CMAQ 5.0.2, and CMAQ 4.7.1. At Oki a substantial photochemical O_3 production was simulated by NAQM and CMAQ 5.0.2 up to more than 15 ppbv hr^{-1} and a smaller amount of less than ca. 10 ppbv by CMAQ 4.7.1 corresponding to the simulated NO_x mixing ratios. Such in-situ net production during daytime shows a distinct diurnal

Fig. 6

298 variation for the simulated mixing ratios of O_3 during a certain period in July. Thus, virtually
299 simulated relatively high NO_x is thought to brought the in-situ photochemical ozone production
300 in the CTMs, which contributes to the overestimate of the monthly-averaged mixing ratio of O_3
301 at Oki by all the three models.
302 An analysis reveals that the situation is similar at Hedo. Photochemical O_3 production up to
303 8-10 ppbv hr^{-1} has been simulated by CMAQ 5.0.2 and 4.7.1 as shown in Fig. 6(b). Although
304 Hedo is also a remote island site, the local emission of NO from sugar cane fields soils emit
305 substantial NO as noted before, which resulting in some daytime O_3 peaks in the observational
306 data as shown in Fig. 3(b). The substantial overestimate of the photochemical O_3 formation at
307 Hedo produced by CMAQ 5.0.2 and 4.7.1 as revealed by the distinct diurnal variation of O_3 in
308 Fig 3b, may be due to the virtual transport of NO_x from urban areas in the southerly part of
309 Okinawa island, as in the case of Oki. The overestimate of the in-situ photochemical buildup of
310 O_3 seems to have resulted from an overestimate of more than ca. 10 ppbv in the monthly mean
311 mixing ratios by these models in addition to the overestimate of the background levels.
312 At Ogasawara, no such photochemical buildup of O_3 can be seen by any of the models, as
313 shown in Fig. 6(c). The negative net ozone production would be due to the O_3 destruction by the
314 photochemical HO_x cycle under very low NO_x conditions (Akimoto, 2016). The overestimate of
315 background O_3 in clean marine air mass gives a value of ca.10 ppbv monthly mean O_3 by the
316 CMAQ models (Fig. 2c).
317
318 **3.4 Dry deposition of O_3 on seawater**
319
320 Figures 7(a)-(c) compare the spatial distribution of monthly mean surface ozone mixing ratios in
321 July 2010 in the coastal and oceanic areas of East Asia calculated by NAQM, CMAQ 5.0.2, and
322 4.7.1, respectively. A large variability in the O_3 mixing ratio among the models can be seen in
323 heavily polluted land areas, and possible causes of the difference in the megacities of Beijing and
324 Tokyo have been discussed in our previous paper (Akimoto et al., 2019). In addition to the land
325 area, a difference of surface O_3 mixing ratios in the oceanic area among the three models can be
326 seen in the figures. The NAQM-simulated surface O_3 in the open oceanic area south of Japan is
327 10-15 ppbv, which is substantially lower than the 25-30 ppbv produced by CMAQ 5.0.2 and 4.7.1.
328 These values correspond well to the monthly mean O_3 mixing ratios at the "true oceanic site"
329 Ogasawara, shown in Fig. 2(c). Figure 7 also shows that Cape Hedo in Okinawa is at the edge of
330 the Pacific marine airmass with the lowest O_3, where the coastal airmass is affected by the
331 continental outflow. The O_3 mixing ratio near this site simulated by CMAQ 5.0.2 and 4.7.1 is 30-
332 40 ppbv as compared to ca. 10-20 ppbv calculated by NAQM, which corresponds well with the
333 monthly mean observational values at Hedo (Fig. 2(b)).

Fig. 7

Thus, the overestimate of surface ozone at the oceanic sites of Hedo and Ogasawara produced by the CMAQ models shown in Fig. 7 are ascribed to an overestimate of O_3 in the vast area of the open Pacific Ocean. We speculate that this overestimate is caused by an underestimate of dry deposition velocity of O_3 on seawater made by these models. Ganzeveld et al., (2009) reported that large uncertainties exist in the magnitude of the air-sea exchange of ozone with the deposition velocity (V_d) ranging from 0.01 to 0.15 cm s^{-1} for oceanic water and 0.01–0.1 cm s^{-1} for freshwater. Typically applied values for V_d over the ocean in global models are in the range of ~0.013 to 0.05 cm s^{-1} [Ganzeveld and Lelieveld, 1995].

Although direct measurements of the ozone deposition flux over the ocean are limited, Helmig et al (2012) conducted a ship-based eddy covariance ozone flux measurement on five cruises covering the Gulf of Mexico, the southern and northern Atlantic, the Southern Ocean and the eastern Pacific along Chile. The median V_d for four cruises falls within the range of 0.01-0.02 cm s^{-1} in the off-coast ocean area, while the median V_d measured in the coastal zone fell within the range of 0.24 ± 0.02 cm s^{-1} (Helmig et al., 2012). Oh et al. (2008) reported a study that focused on the effect of dry deposition of O_3 on the ocean in the northwestern Gulf of Mexico using CMAQ. A modified module including iodide reaction showed a significant increase in the velocity of the dry deposition of O_3 onto the sea surface.

In order to discuss the effect of dry deposition of O_3 over the seawater, the spatial distribution of monthly-averaged V_d in the continental rim region of the Northwest Pacific Ocean was simulated by NAQM, CMAQ 5.0.2, and 4.7.1 in Fig. 8(a)-(c), respectively. The simulated V_d of O_3 has been calculated by

Fig. 8

$$V_d = \frac{F_{O3}}{[O_3]} \quad (1)$$

where F_{O3} is the downward deposition flux of O_3 (ppbv s cm^{-1}) and [O_3] is the monthly mean surface O_3 mixing ratio (ppbv). Figure 9 shows that the V_d over the Northwestern Pacific Ocean south of Japan is typically 0.0015-0.002 cm s^{-1} in the NAQM simulation and 0.0005-0.001 cm s^{-1} in the CMAQ 5.0.2, and 4.7.1 simulations. Thus, the values used by NAQM are about twice as large as those used by CMAQs. Although even the values used by NAQM are nearly one order of magnitude smaller than the measured values (0.01-0.02 cm s^{-1}) in the Atlantic open ocean by Helmig et al. (2012), the better reproduction of observed O_3 mixing ratios at Hedo and Ogasawara by NAQM simulations may be ascribed to a twice as large deposition velocity as that in CMAQs. The dry deposition velocity of O_3 in the global models used in MICS-Asia III is based on Wesley (1989), and the value of ~0.045 cm s^{-1} has been adopted over Pacific Ocean for both GEOS-Chem and CHASER. Thus, at the moment there is a large gap between the deposition velocities used in the global and regional models, which are substantially larger and smaller than the observed value in the Atlantic Ocean, respectively. Future accommodation by obtaining the observation in the

Pacific Ocean is required to solve the issue.

It can be noted that the mixing ratios of O_3 in the Bohai Bay and the Yellow Sea shown in Figs. 8a-c are relatively high for all the three models as compared to the surrounding land area. This may be caused by the use of a much smaller deposition velocity of O_3 over the ocean closer to the continent. While iodine has been estimated to be most important in increasing the dry deposition velocity of O_3 over the ocean, dissolved organic carbon is also thought to contribute significantly to this process (Ganzeveld et al., 2009; Sarwar et al, 2015). Coleman et al. (2010) also showed that in addition to iodide the inclusion of dissolved organic compounds (DOC) described daytime deposition observation better in coastal water of the North Atlantic. Thus, the dry deposition velocity of O_3 in the Bohai Bay and the Yellow Sea is expected to be much higher than that in the open Pacific Ocean. However, as shown in Fig. 8, the dry deposition velocity in this area employed by all the three models is even smaller than that in the open Pacific Ocean. This is unreasonable considering the discussion by Ganzeveld et al. (2009) which has been supported by the findings of Helmig et al. (2012). Particularly, the even lower deposition velocity in this area assumed by NAQM compared to that in the open Pacific may have contributed substantially to the overestimate of O_3 at Oki by this model. The amount of long-range transport of O_3 is in general affected by the mixing ratios of both in the boundary layer and free troposphere. Although the assessment of the contribution of each is beyond the scope of this study, the overestimate of O_3 mixing ratio in the MBL of Bohai Bay and Yellow Sea would contribute to the overestimate of transboundary long-range transport of O_3 to Oki, and mainland of Korea and Japan to a certain extent. Since the model is highly sensitive to water surface resistance, it is important to empirically obtain the values of dry deposition flux of O_3 and its precursors over the Bohai Bay and the Yellow Sea.

In addition to the dry deposition on sea water, photochemical gas-phase halogen chemistry mainly by bromine and iodine has been suggested to decrease surface O_3 in the marine boundary layer in the northern hemisphere (Sarwar et al., 2015). Nagao et al. (1999) reported the 10-15% loss of surface O_3 in May-October based on the observation at Ogasawara throughout a year, which they ascribed to the bromine released by heterogeneous reaction of sea salt. Read et al. (2008) reported eight months of spectroscopic measurements of BrO and IO at the Cape Verde Observatory in tropical eastern North Atlantic, and evaluate the annual average daily ozone loss of 3.2±1.1 ppbv d^{-1}, which amounts to 50 % greater than that simulated by a global chemistry model excluding halogen chemistry. Mahajan et al. (2010) also estimated that the calculated O_3 depletion in the marine boundary layer at Cape Verde Islands increases to ~4.5 ppbv d^{-1} by including the halogen chemistry compared to ~2.5 ppbv d^{-1} due to HO_x chemistry and deposition to the ocean surface.

Since the present versions of CMAQ and NAQM do not include gas-phase chemistry of

halogens, the monthly averaged O_3 mixing ratios simulated by these models as shown in Fig. 2 would decrease a couple of ppbv according to the above studies (Nagao et al., 1999; Read et al., 2008; Mahajan et al., 2010). This would improve the agreement of the simulated results of CMAQ 4.7.1 and 5.0.2 with observation at Hedo and Ogasawara, but lead to underestimate of that of NAQM to some extent.

Since no sensitivity analysis of the impact of dry deposition velocity and gas-phase halogen photochemistry has been made in MICS-Asia III, future studies will be necessary to resolve the issue.

4 Future Research Recommendations

The present and the previous paper (Akimoto et al., 2019) aimed to elucidate the causes of discrepancies of surface-level ozone at remote marine sites and central megacity sites in East Asia, respectively, among models and between models and observation. Based on the findings in these analyses, a couple of future research recommendations are proposed here in order to solve the issues encountered in model intercomparison studies on surface-level ozone.

1. Measurement of the mixing ratios and dry deposition flux of O_3 over the Bohai Bay and the Yellow Sea

   Surface-level ozone mixing ratios in the marine region of East Asia have been found to be sensitive to the dry deposition velocity of O_3 over seawater. Although the dry deposition velocity over the Bohai Bay and the Yellow Sea is expected to be much larger than that over the open ocean in the Northwestern Pacific due to the enriched organic compounds brought by rivers and atmospheric wet deposition, no such measurements have been conducted to our knowledge. Since the dry deposition velocity of O_3 over the Bohai Bay and the Yellow Sea may affect the evaluation of trans-boundary transport of O_3 to the down-wind region, the measurement of the mixing ratios and V_d of O_3 in this marine area is highly recommended.

2. Simultaneous comprehensive measurement of NO_y focusing on gaseous HNO_3 in urban areas

   In order to perform reliable model simulation of surface-level ozone in urban areas for the purpose of proposing an ozone control policy, it is important to verify if NO_y chemistry is properly incorporated. In particular, model validation for HNO_3 is important, since the mixing ratio of gaseous HNO_3 is estimated to be comparable to NO_x. However, due to technical difficulty, direct measurement of gaseous HNO_3 together with other NO_y has rarely been conducted. Field campaign in urban areas for simultaneous measurement of NO_y including direct measurement of gaseous HNO_3 (e.g. by chemical ionization mass spectrometry) is highly recommended focusing on the quantification of the potential importance of the heterogeneous “renoxification” reaction of HNO_3 to regenerate NO_x on the aerosol surface.

These activities are recommended to be jointly co-organized by field experimentalists and modelers.

5 Summary

Simulations by the regional chemical transport models, NAQM, CMAQ v.5.0.2 and CMAQ v.4.7.1, in the context of MICS Asia III overestimated the observed surface-level ozone at Oki in July 2010 by 20-30 ppbv. In order to identify the causes of this overestimate, analyses were performed not only for Oki but for two other EANET marine sites, Hedo and Ogasawara as well. At Hedo and Ogasawara, NAQM reproduced reasonably well the observational values of monthly mean diurnal mixing ratios of O_3, while the two CMAQ models overestimated the observation by 23-27 ppbv and 11-14 ppbv, respectively.

Three factors have been identified as the possible cause of overestimate made by the model simulations at Oki; (i) long-range transport of O_3 from the continent, (ii) in-situ photochemical formation of O_3, and (iii) dry deposition of O_3 on seawater. An overestimate of transported O_3 from the continent can be identified at Oki in July for all the three models. The overestimate for the CMAQ models may partly be ascribed to an overestimate of the O_3 mixing ratio in the source region of China. An overestimate of long-range-transported O_3 was also seen in NAQM which reproduced the mixing ratio in Beijing reasonably well. The cause of overestimate of long-range-transported O_3 by NAQM may partly be ascribed to the possible overestimate of the marine boundary layer O_3 in Bohai Bay and Yellow Sea due to the too small deposition velocity of O_3 over the seawater assumed in the models.

The overestimate of the monthly-averaged mixing ratio of O_3 at Oki has been ascribed partly to the in-situ photochemical formation, which was demonstrated by the distinct diurnal variation of O_3 produced by all the three models but not discernible in the observational data. Such an in-situ formation of O_3 was found to be caused by the virtual transport of NO_x in the model simulation from the urban areas of mainland Japan to Oki.

At Hedo and Ogasawara sites, an overestimate of O_3 in the oceanic air mass was found in CMAQ 5.0.2 and 4.7.1, while a reasonably good agreement with observational data was obtained by NAQM. The overestimate by the CMAQ models was ascribed to the employment of too small dry deposition velocity of O_3 on seawater, while the use of a larger deposition velocity by NAQM may have resulted in a better agreement with the observation. It has been identified that O_3 mixing ratios over the Bohai Bay and the Yellow Sea are higher than those over the surrounding land surface for all the three models, which was ascribed to the employment of too small dry deposition velocity on seawater in this area in spite of higher contents of organics due to the deposition from the atmosphere and rivers.

Data availability. The EANET observational dataset used in this study is available at http://www.eanet.asia.

Author contributions. HA analyzed the data and wrote the first draft of the paper. TN, JL, and JSF provided the model simulation data for their own models and conducted discussions for the paper. ZW contributed to the availability of modeling data as a coordinator of MICS-Asia III.

Competing interests. The authors declare that they have no conflict of interest.

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Review statement.

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Figures

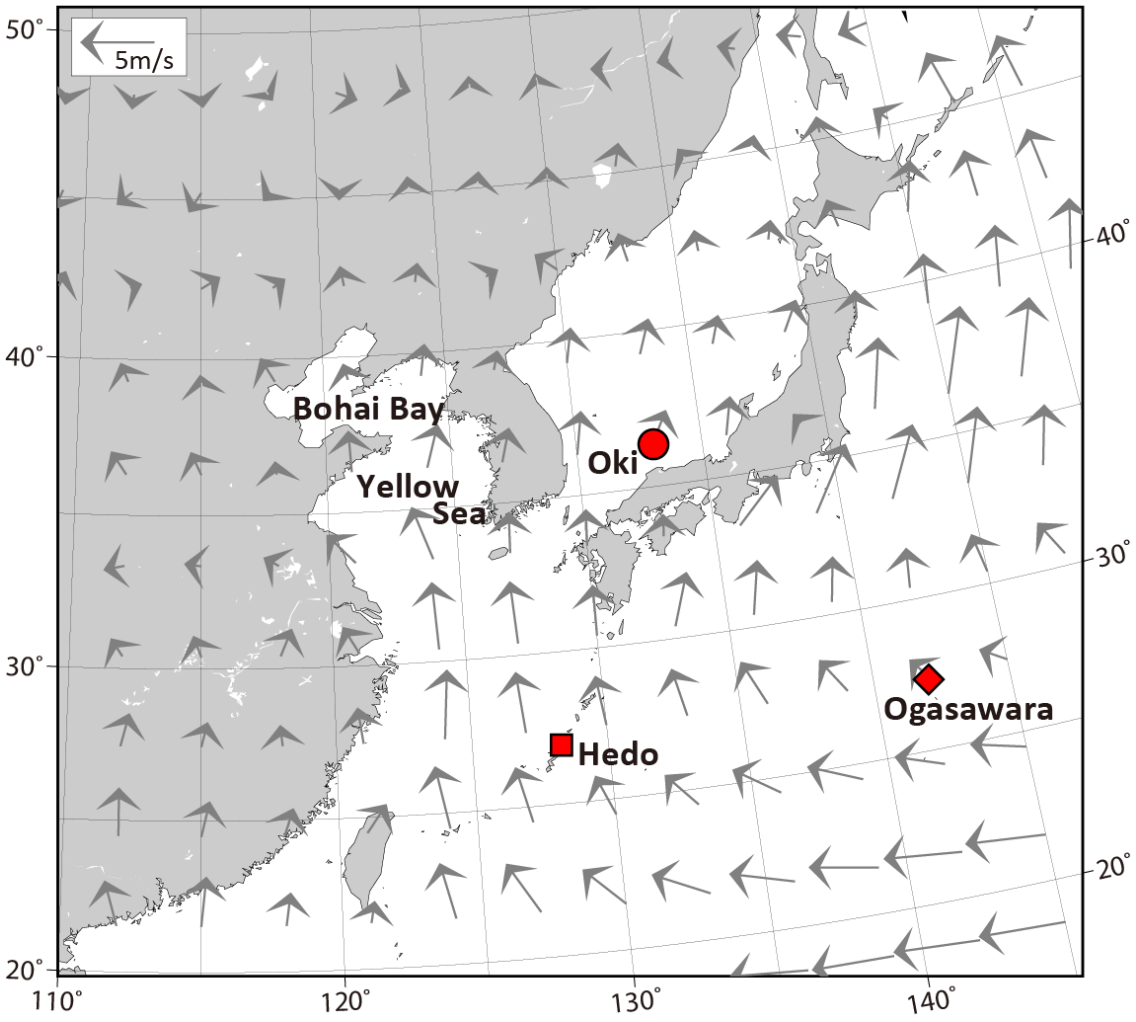

Fig. 1 Locations of EANET observation sites at Oki (circle), Hedo (rectangle) and Ogasawara (diamond). Vectors show monthly mean surface wind velocity in July.

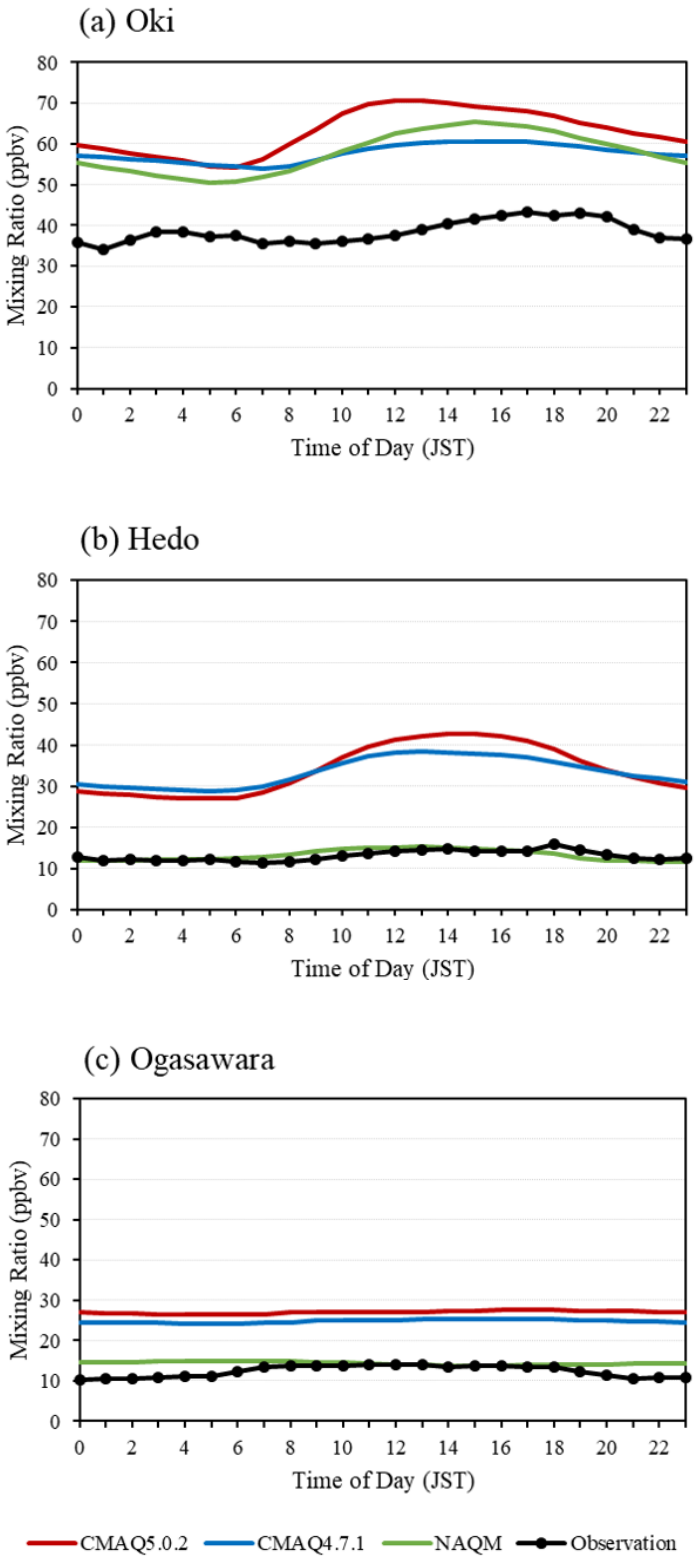

Fig. 2 Comparison of monthly-averaged diurnal variation of O_3 at (a) Oki, (b) Hedo, and (c) Ogasawara in July 2010 between observation and model simulation by CMAQ v.5.0.2 and 4.7.1, NAQM v.3.

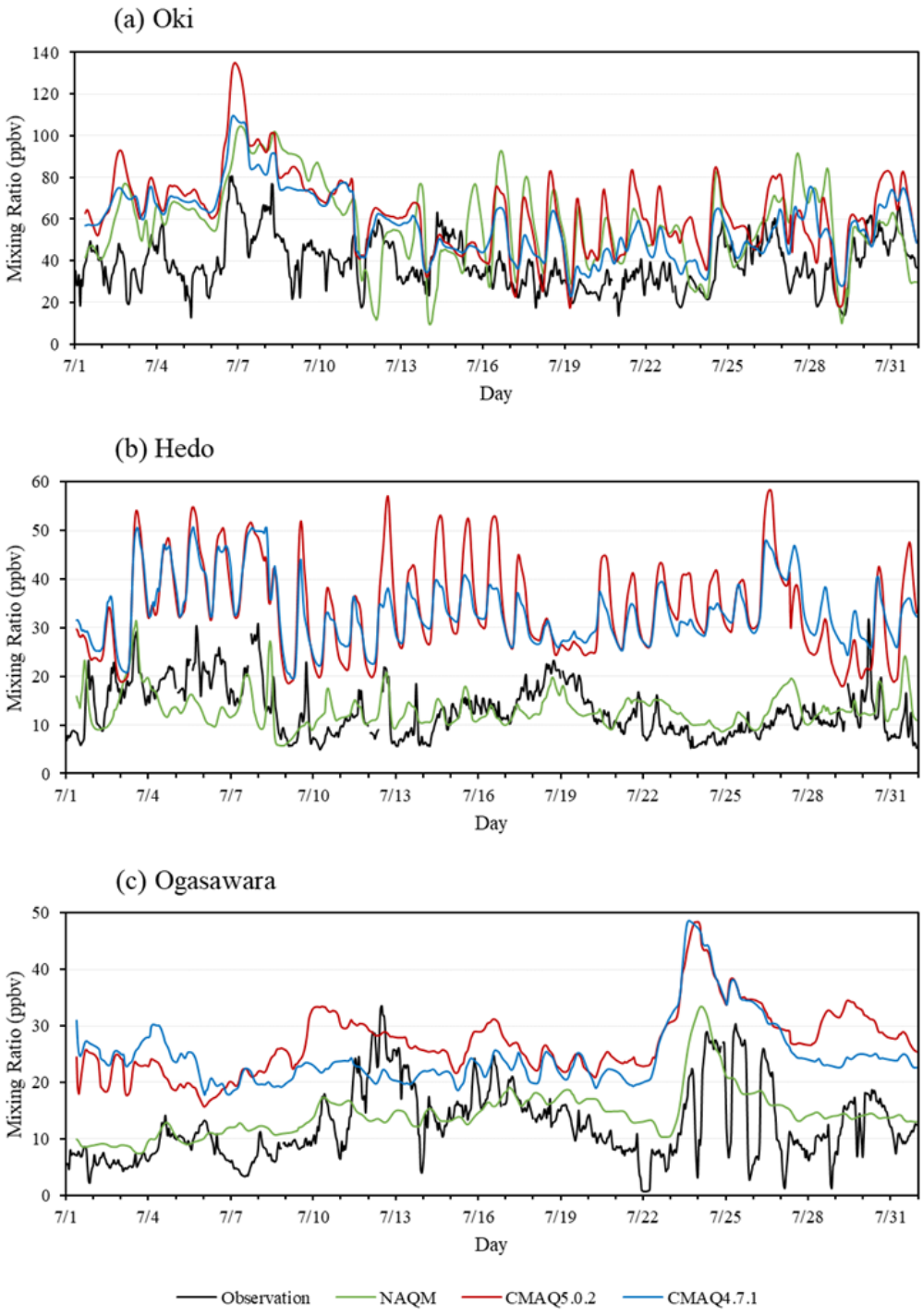

Fig. 3 Comparison of diurnal variation of surface O_3 mixing ratios at (a) Oki, (b) Hedo, and (c) Ogasawara in July, 2010 between observation and model simulation by CMAQ v.5.0.2 and v. 4.7.1 and NAQM v.3. Note that vertical scale is different for Oki and

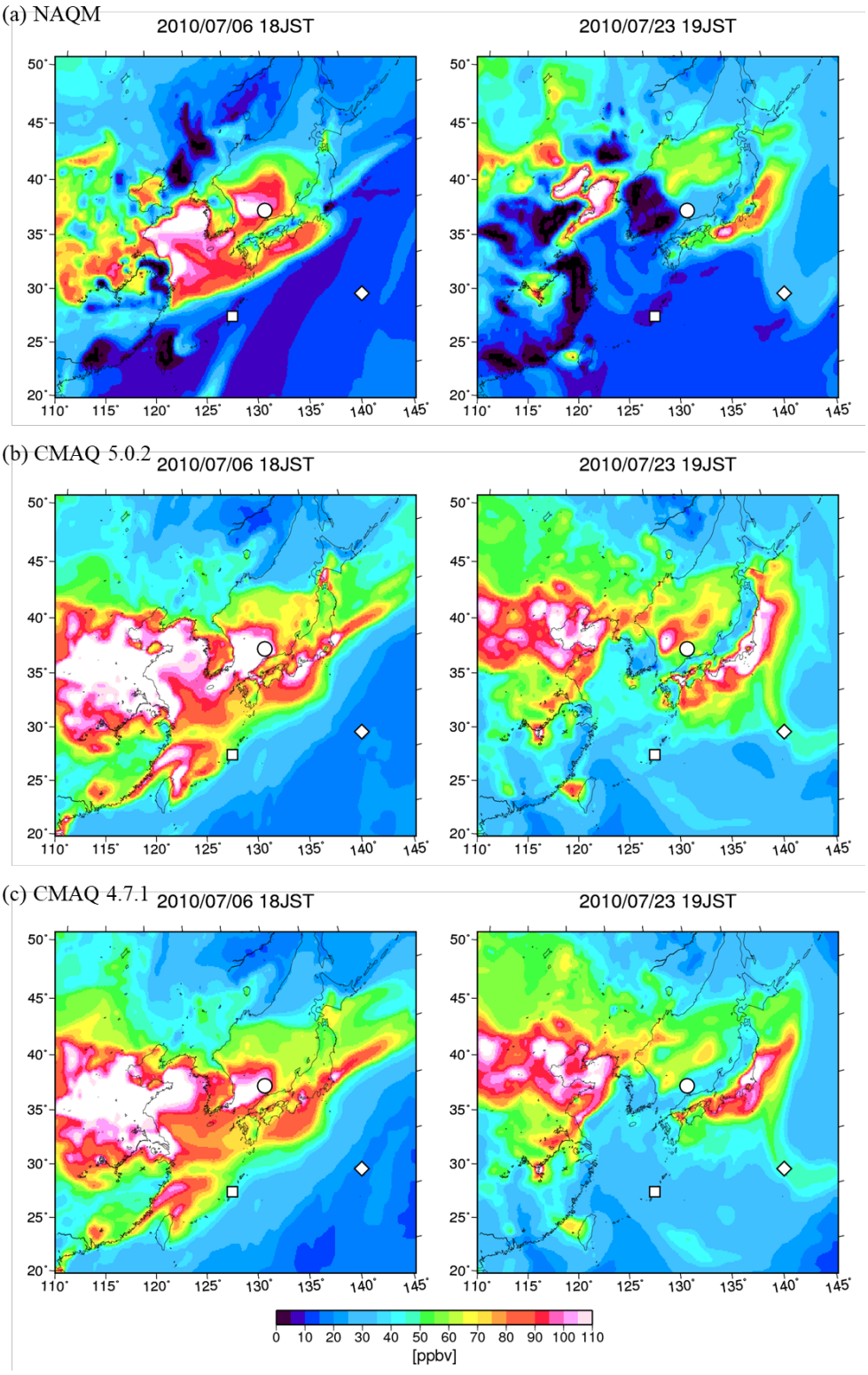

Fig. 4 Spatial distribution of surface O_3 over Northeast Asia at 18 JST on July 6 (left) and 19 JST on July 23 (right), 2010 simulated by (a) NAQMS, (b) CMAQ 5.0.2 and (c) CMAQ 4.7.1. Markers denote the location of observation sites.

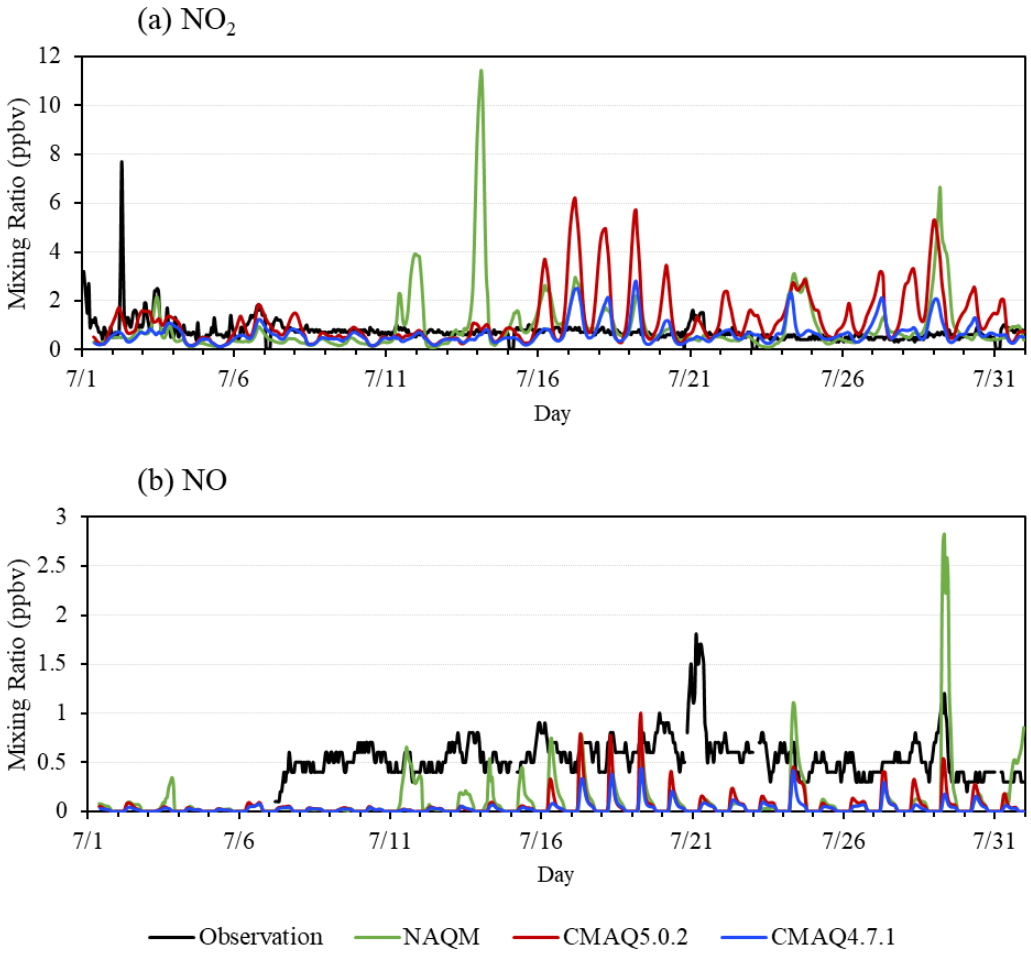

Fig. 5 (a) Mixing Ratios of NO_2* by observation, NO_2 by NAQM, CMAQ v.5.0.2, and CMAQ v. 4.7.1 at Oki in July 2010. (b) Same as (a) but for NOThe sharp peak of NO_2 on July 2 would be an artifact or influence of accidental local pollution (see text). The observed concentration of NO in the first week of July is in general under the detection limit and deleted from the figure.

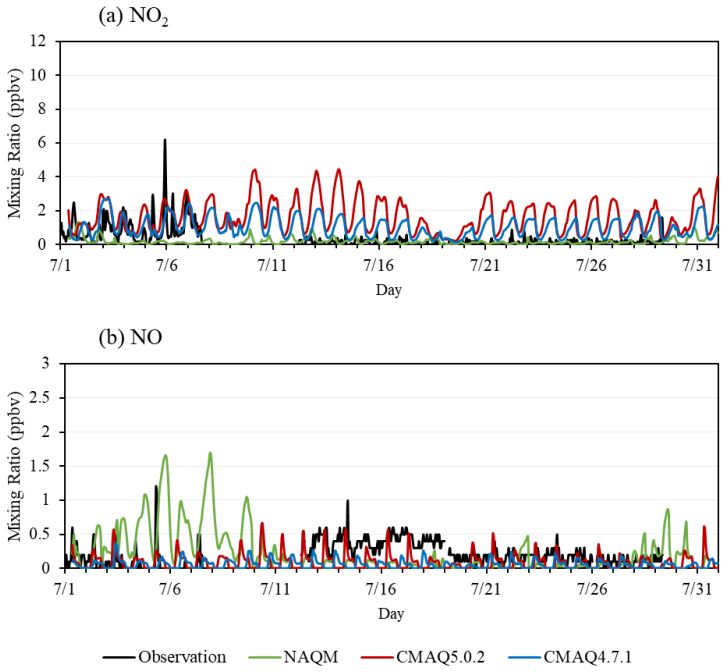

Fig. 5S-1 (supplement) (a) Mixing Ratios of NO_2* by observation, NO_2 by NAQM, CMAQ v.5.0.2, and CMAQ v. 4.7.1 at Hedo in July 2010. (b) Same

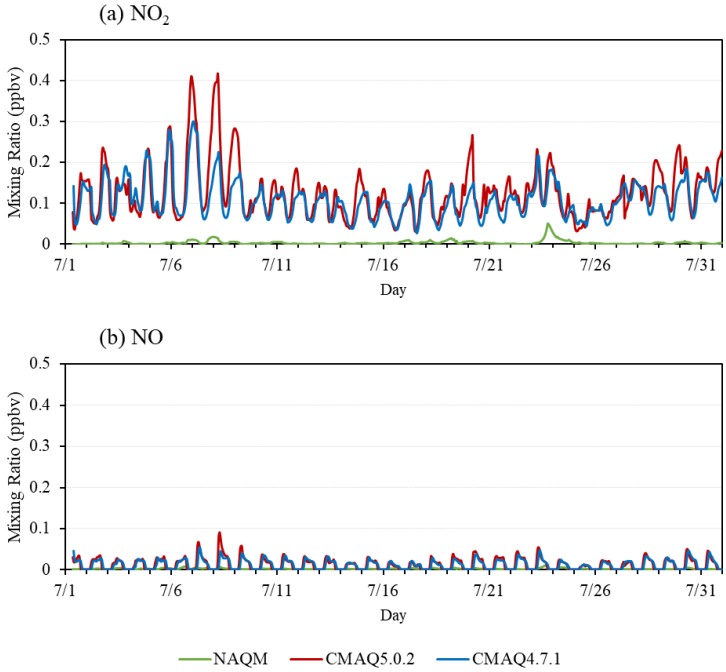

Fig. 5S-2 (supplement) (a) Mixing Ratios NO_2 by NAQM, CMAQ v.5.0.2, and CMAQ v. 4.7.1 at Ogasawara in July 2010. (b) Same as (a) but for NO.

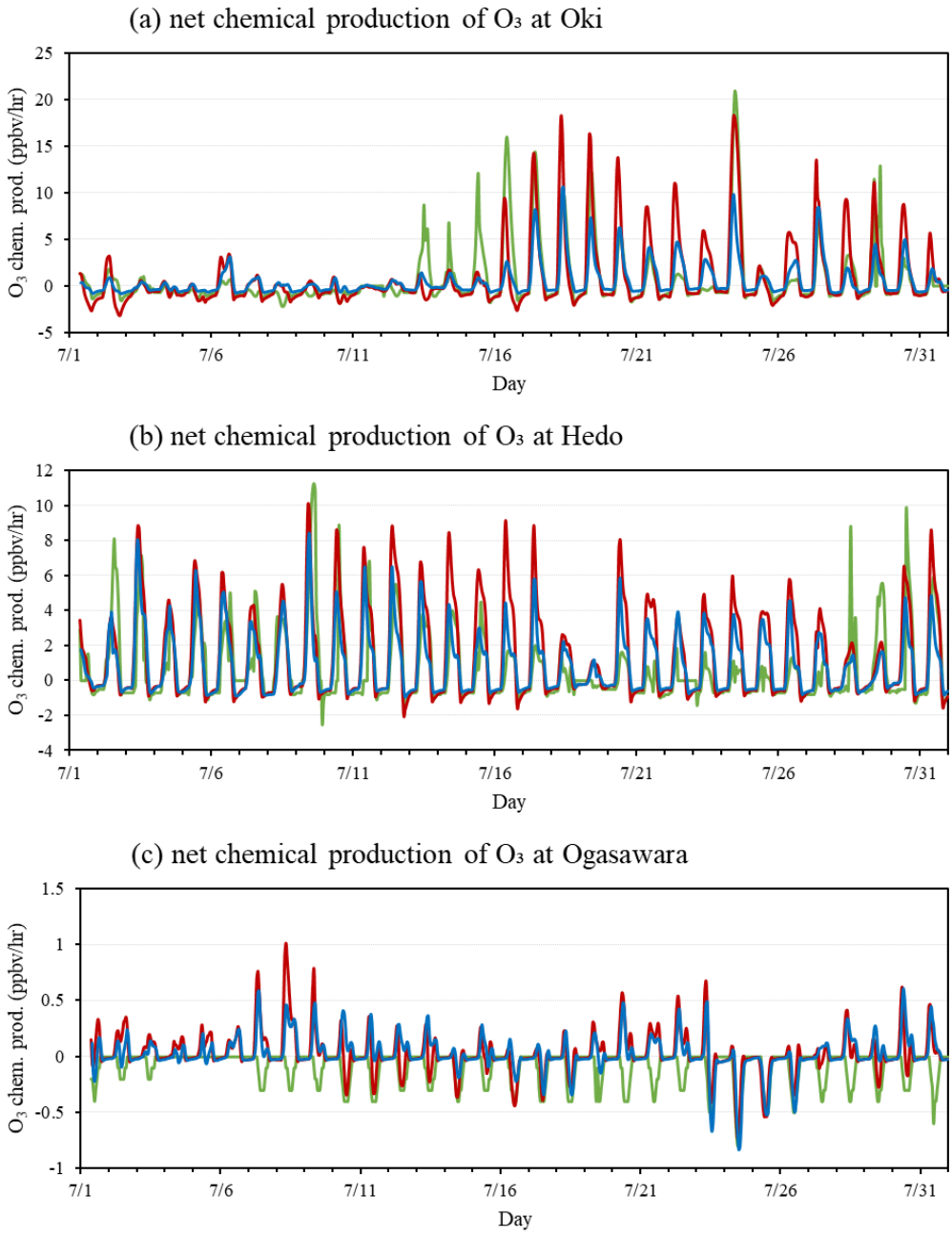

Fig. 6 Model-calculated net chemical production of O_3 in July 2010 by NAQM, CMAQ5.0.1 and CMAQ 4.7.1. at (a) Oki, (b) Hedo and (c) Ogasawara.

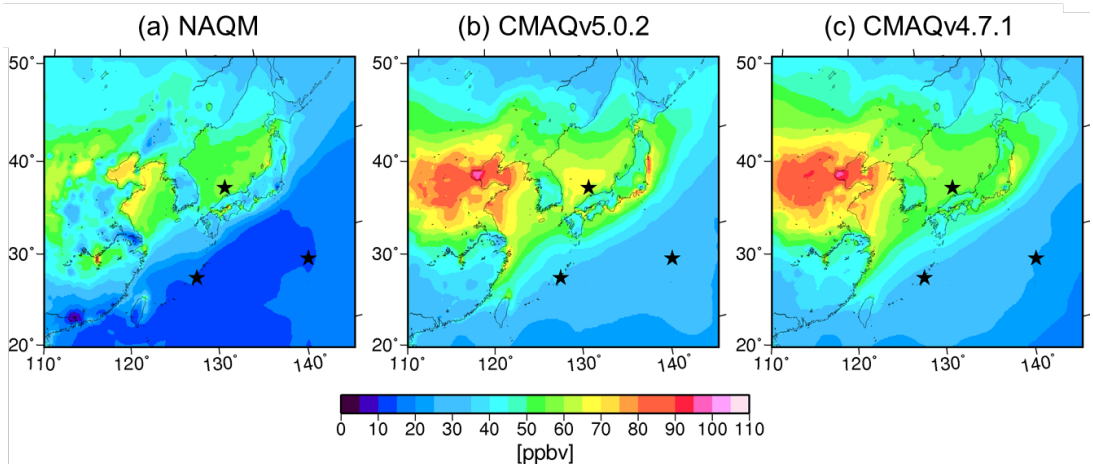

Fig. 7 Comparison of spatial distribution of surface O_3 mixing ratios in East Asia in July simulated by (a) NAQM, (b) CMAQ 5.0.2, and (c) 4.7.1.

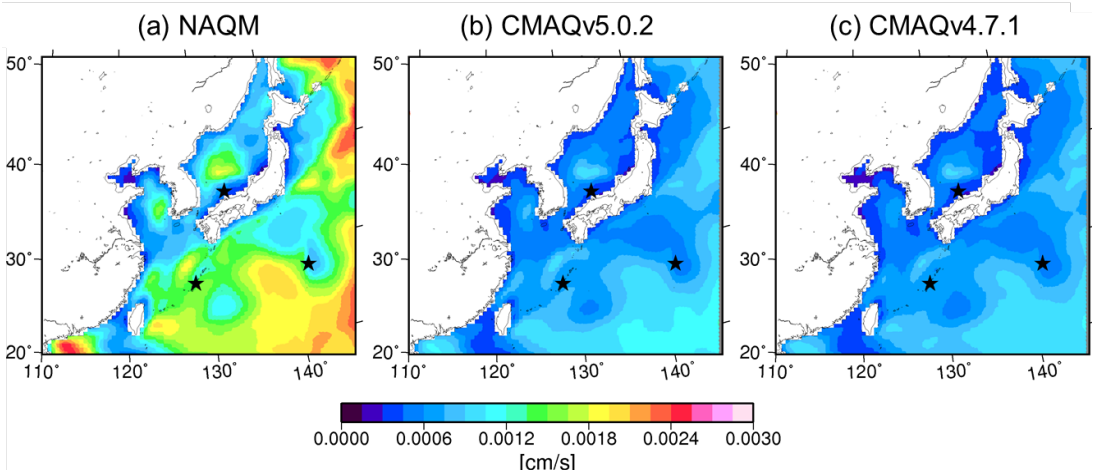

Fig. 8 Comparison of spatial distribution of dry deposition velocity of O_3 in East Asia simulated by (a) NAQM, (b) CMAQ 5.0.2, and (c) 4.7.1.